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DEFENCE SCIENCE AND TECHNOLOGY ORGANISATION
MATERIALS RESEARCH LABORATORY
MELBOURNE, VICTORIA

REPORT

MRL-R-1145

CORROSION OF HIGH-DENSITY SINTERED TUNGSTEN ALLOYS
PART 2: ACCELERATED CORROSION TESTING


J.J. Batten and B.T. Moore

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**CORROSION OF HIGH-DENSITY SINTERED TUNGSTEN ALLOYS
PART 2: ACCELERATED CORROSION TESTING**

J.J. Batten and B.T. Moore

ABSTRACT

As a consequence of corrosion during long-term storage in uncontrolled environments, where high humidity may be combined with cyclic temperature changes, some high-density sintered tungsten penetrators have been found to be unreliable. A storage life of twenty years without special storage conditions is a requirement for this ammunition, and therefore there is a need to determine the long-term storage capability of selected alloys.

The corrosion behaviour of four candidate alloys has been evaluated and compared with that of pure tungsten. Rates of corrosion during the Cyclic Humidity Test and the Salt Mist Test were ascertained from weight loss measurements. Insight into the corrosion mechanism was gained from the nature of the corrosion products and an examination of the corroded surfaces. In the tests, the alloy 95% W, 2.5% Ni, 1.5% Fe was the most corrosion resistant. The data showed that copper as an alloying element accelerates corrosion of tungsten alloys. Both attack on the tungsten particles and the binder phase were observed together with tungsten grain loss. *Keywords: Corrosion resistant alloys, Corrosion, (167)*

The propensity of the above alloy to corrode when encapsulated and also when enclosed by its ammunition box was also evaluated. Conclusions and recommendations regarding the corrosion of tungsten alloy penetrators for use in ammunition are offered.

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CORROSION OF HIGH-DENSITY SINTERED TUNGSTEN ALLOYS

PART 2: ACCELERATED CORROSION TESTING

1. INTRODUCTION

High-density sintered tungsten alloys (W \geq 90 wt%) for kinetic energy penetrators must be capable of withstanding long-term storage without special storage conditions (uncontrolled environment) where high humidity may be combined with cyclic temperature changes. It is essential that the material does not undergo any degradation in mechanical or ballistic properties due to corrosion during storage. Currently there is no agreed storage life under the above conditions for these alloys [1,2,3].

We have shown previously [4] that the alloy 95% W, 3.5% Ni, 1.5% Fe had the greatest corrosion resistance of four candidate alloys when fully immersed in water and in 5% sodium chloride solution. Work [1,2,3] concerned with exposure of these alloys to air saturated with water vapour has indicated that they are prone to corrosion under such conditions, and that the course of the reaction is profoundly influenced by the chemical composition of the binder, the nature of the corrosive environment and the presence of crevices. These results have indicated that the binder phase and/or the primary tungsten grain phase may be attacked, often severely, and that tungsten grain loss may occur.

Although the corrosion of these tungsten alloys had not been considered a problem, because of the above work it is now necessary to reassess the situation. An evaluation of the long-term storage capability of these alloys, without resorting to special storage conditions, has therefore been carried out. Bare alloys (i.e. alloys whose surfaces are freely exposed to the environment) were subjected to accelerated corrosion through the Cyclic Humidity and the Salt Mist Tests [5]. However, in normal storage these alloys may be encapsulated (see Experimental) and further, in this state, they may also be stored in a sealed steel ammunition box. Thus, the Cyclic Humidity Test was also carried out on the alloy 95% W, 3.5% Ni, 1.5% Fe in these two practical storage modes.

2. EXPERIMENTAL

2.1 Accelerated Corrosion Testing of Bare Tungsten Alloys

2.1.1 General procedure

Four candidate tungsten-based alloys were selected for this study, and for comparative purposes pure tungsten was also studied. Details of these materials, the method of preparation of the samples prior to testing and the method of removing corrosion products from the samples after the tests have been described previously [4]. Corrosion behaviour was evaluated through weight loss measurements, the nature of the corrosion products and an examination of the corroded surfaces using a scanning electron microscope (SEM).

2.1.2 Accelerated corrosion tests

- (a) **The Cyclic Humidity Test (I5), Test Db)**
The components are exposed at controlled temperatures (in the range 25 to 40°C) and at high relative humidity (in the range 93 to 96%) for 56 cycles (12 + 12 hour cycle) with condensation on the specimens occurring during the temperature-rise period. The upper and lower temperatures were maintained for about 9 hours each, the remaining 6 hours of the cycle being occupied by the transition periods between these two extremes of temperature.
- (b) **The Salt Mist Test (I5), Test Kb)**
The components are exposed to a salt solution mist for 2 hours at a temperature of $20 \pm 5^\circ\text{C}$, and then stored at a temperature of $35 \pm 2^\circ\text{C}$ at a relative humidity of between 90 and 95%. The severity used was four spraying periods with a storage of 7 days after each (severity 1).

Both accelerated tests were conducted in a computer-controlled humidity cabinet in which duplicate specimens were suspended by nylon threads and beakers were placed under the specimens to collect corrosion debris.

Two types of corrosion specimens were used, namely 3 mm thick discs (about 25 mm diameter) for the alloys US, UK (Fe) and UK (Cu), while short cylinders (about 12 mm diameter) were used for AUS. With the Cyclic Humidity Test, comparisons between samples are valid only when each receives about the same amount of condensation. Each therefore needs about the same heat capacity, and for this reason the weights of the samples were kept approximately equal.

2.2 Cyclic Humidity Testing on Encapsulated Tungsten Penetrators

2.2.1 Penetrators not enclosed in an ammunition box

This test involved actual Australian-produced Phalanx rounds where the tungsten penetrator is completely encapsulated by the nylon discarding sabot and the aluminium pusher. Prior to the test measurements were taken of

- (a) the individual weights of (i) the penetrator, and (ii) the nylon discarding sabot, and

- (b) the diameter of the assembly (i) across the sabot, and (ii) across the driving band.

2.2.2 Penetrators enclosed in the appropriate ammunition box

In these Cyclic Humidity Tests the encapsulated penetrators were enclosed in a steel ammunition box (the M548) in which a seal between the lid and the body of the box was created by a rubber gasket. The whole of the box was placed in the humidity cabinet.

2.2.3 Penetrators enclosed in the appropriate ammunition box but in the presence of a high humidity environment

The above Cyclic Humidity Test was repeated but, in this experiment, between the 3rd and 6th cycles of the 56-cycle test the lid of the box was removed. This lid was replaced at a time in the cyclic sequence when condensation was at its greatest.

3. RESULTS

3.1 Accelerated Corrosion Testing of Bare Tungsten Alloys

3.1.1 Corrosion behaviour during the Cyclic Humidity Test (Test Db)

3.1.1.1 Corrosion rate

These corrosion rates are listed in Table 1 which shows that pure tungsten was the most corrosion resistant (no corrosion was detected), followed by alloys not containing copper and alloys containing copper in order of decreasing merit. This test is designed specifically to determine the long-term storage capability of metallic stores under conditions of high humidity when combined with cyclic temperature changes [6]. This type of corrosive environment is typical of that which can develop in packages during long-term storage unless special precautions are taken. Under these circumstances the extent of corrosion of the US alloy and the UK (Cu) alloy would be clearly unacceptable. In fact, the need for this work arose because of the poor corrosion resistance of the UK (Cu) alloy during long-term storage under high humidity conditions [1,2]. This result has confirmed this poor performance.

3.1.1.2 Nature of the corrosion process

An insight into the nature of this process is revealed through a study of the products formed during the reaction together with a SEM examination of the corroded surfaces after the corrosion products have been removed. The conditions of the various tungsten alloys after Test Db are shown in Figure 1 and described in Table 1. All the alloys suffered corrosion to varying extents. The extent of this corrosion can be seen for the alloys US and UK (Cu), where a viscous dark grey or dark green (respectively) corrosion product dropped from the suspended specimens and solidified to a glossy

cracked solid by the completion of the test - in the photographs (Fig. 1) the test specimens have been placed next to their respective corrosion products on the bottom of the beaker. Note that the two alloys that dripped corrosion products both contained copper.

The nature of the corrosion processes occurring during the Cyclic Humidity Test are indicated by the chemical compositions of the corrosion products (Table 1). For example,

- (a) The high percentage of tungsten in the corrosion products together with binder metals indicates that the matrix phase and the primary tungsten grain phase are corroding.
- (b) The ratios Ni to Fe and Ni to Cu in the parent alloy and in the corrosion products are virtually identical, hence there has not been any preferential attack on elements.
- (c) By comparing the composition of the corrosion products with that of the original alloy the following observations may be made. First, with alloys AUS, US and UK (Fe) the binder has been more severely attacked than the primary tungsten grains. Secondly, with the UK (Cu) alloy, the primary tungsten grains are being attacked at much the same rate as the binder.

The above deductions are confirmed by the SEM micrographs of the corroded surfaces (Fig. 2), where the interpretation of these micrographs is summarized in Table 1. The mode of attack has varied between the alloys: it has ranged from little (if any) attack on the tungsten grains, to extensive attack and ultimately to tungsten grain loss and grain boundary attack of the tungsten particles. For all the alloys the binder phase appears to have been attacked. Broadly the state of the corroded surfaces can be grouped by their appearance into the categories, those alloys containing copper (US and UK (Cu)) and those not containing copper (AUS and UK (Fe)), where the overall extent of attack for the former group is more extensive than that for the latter.

3.1.2 Corrosion behaviour during the Salt Mist Test (Test Kb)

3.1.2.1 Corrosion rate

This test is designed to determine the suitability of components for use or storage in a salt-laden atmosphere. Corrosion rates are listed in Table 2. Comparison of these rates with those in Table 1 indicates that they are considerably less than those arising from the Cyclic Humidity Test - in fact they approximate those arising from the immersion in salt-solution test [4]. In contrast, however, for tungsten itself the rate from the Salt Mist Test is considerably greater than that arising from the two tests mentioned above. Further, in the Salt Mist Test, pure tungsten is more prone to corrode than the alloys AUS and UK (Cu).

3.1.2.2 Nature of the corrosion process

The conditions of the various tungsten alloys and of tungsten itself after the Salt Mist Test are shown in Figure 3 and described in Table 2. All the alloys have suffered corrosion to varying extents during the test but corrosion products have not dripped from the samples.

From the chemical compositions of the corrosion products (Table 2) the following deductions can be made concerning the nature of the corrosion process.

- (a) The distribution of elements in the products indicates that the primary tungsten particles and the binder phase are corroding.
- (b) The high concentration of elements from the binder phase in the products (in particular for AUS and UK (Fe)) indicates that the binder phase is being attacked more severely than the primary tungsten grains.
- (c) For AUS and UK (Fe), the ratio of Ni to Fe indicates that the binder phase is not being uniformly attacked and Fe is being leached from the binder. This is consistent with the colour of the corrosion products.
- (d) For US and UK (Cu), the ratio of Ni to Cu indicates that these elements in the binder are being attacked at about the same rate.

Inspection of the SEM micrographs of the corroded samples (Fig. 4) reinforce the above conclusions (see Table 2). In general, polishing marks are still evident on the surfaces of the primary tungsten grains indicating that the extent of attack on this surface has not been extensive. The binder phase, however, has been more severely attacked.

3.2 Cyclic Humidity Testing on Encapsulated Tungsten Penetrators

3.2.1 Penetrators not enclosed in an ammunition box

It would be expected that the encapsulation would afford some protection to the tungsten, although it is quite well known that water vapour will diffuse through nylon. Further, our tests have shown that the heat seal of the nylon sabot to the aluminium pusher provides only a physical barrier and that there is no adhesion between these two components. The tungsten penetrator is, therefore, not hermetically sealed from the external environment.

The purpose of this test, therefore, was to ascertain whether complete Phalanx tungsten (AUS alloy) rounds would withstand long-term storage. The results of subjecting these rounds to the above test were as follows:

- (a) The diameter across the nylon sabot (Fig. 5(a)) was unchanged but the sabot increased in weight by 65 mg (i.e. 0.07% increase). After three weeks standing in the laboratory this increase dropped to 35 mg (0.04%), and after 3, 6, 9 and 12 months the increase had dropped to 13, 6, 3 and 1 mg respectively.
- (b) The diameter of the nylon driving band increased by 0.05 mm (equivalent to a 0.25% increase in diameter), and remained constant during the 12-month period after the test. The driving band is located about half-way up the length of the aluminium pusher (see Fig. 5).
- (c) The tungsten penetrator itself was corroded (see Fig. 5(b), lower). There was a weight gain of up to 8 mg but, after removing the corrosion products, a weight loss of up to 19 mg. Thus the weight of the corrosion products was about 27 mg. This corresponds to a corrosion rate of 0.2 mil/year (i.e. about a fifth of that of the bare alloy).

- (d) The corrosion products (80% W, 13% Ni, 7% Fe) are similar to those obtained from the Cyclic Humidity Test on the bare Australian alloy (cf. Table 1).

Comparison of these Effects with Tolerances allowed by the Specification

- (a) The penetrator (sintered tungsten alloy AUS)

Mass 68.0 ± 0.5 g
Diameter 0.470 ± 0.001 "

Surface finish CLA 63 microinch (in metric units: N7)

Comment: Weight increase due to corrosion (8 mg) and the increase in diameter and surface roughness so produced may place these properties outside those of the specification.

- (b) Driving band (nylon)

Diameter Tolerance is ± 0.001 "

Comment: Increase in diameter of 0.05 mm (0.002") places it outside that of the specification.

- (c) Discarding sabot (nylon)

Mass 9.85 ± 0.15 g (approximately)
Diameter 0.786 (+ 0.000")
 (- 0.003")

Comment: The increase in weight (0.065 g) could be significant, but of greater concern is the very strict tolerance on the maximum diameter.

- (d) Inspection during storage

The policy of the Australian Directorate of Naval Ordnance Inspection and Design, with respect to corrosion occurring during storage, is to remove corroded rounds from service for refurbishment.

3.2.2 Penetrators enclosed in the appropriate ammunition box

After carrying out the Cyclic Humidity Test on the complete Phalanx rounds (AUS alloy), where the rounds were protected from the damp conditions of the test by being enclosed in the appropriate steel ammunition box, the penetrator was still in pristine condition (see Fig. 5(b), centre, left). The above arrangement, therefore, appears to be a satisfactory way of storing these penetrators for long periods.

3.2.3 Penetrators enclosed in the appropriate ammunition box, but in the presence of a high humidity environment

The aim here was to simulate the service conditions where a sealed ammunition box is opened in a humid environment, then closed again, and returned to store for an extended period so that the ammunition is stored in that humid environment. This could be typical of the history of ammunition that is used (but not fired) in exercises and then returned to store. To this end the above trial was repeated but with the inclusion of a 4-day period early in the 56-day test where the lid of the ammunition box was open inside the humidity cabinet.

After the above test the tungsten penetrator was found to be corroded (see Figs. 5(b) and (c), centre). The average weight loss of the penetrators, after removing corrosion products, was found to be 19 mg and this corresponds to a corrosion rate of 0.2 mil/year. This result is identical with that obtained for encapsulated penetrators that are not enclosed in the appropriate ammunition box for any part of the 56-cycle test (see Section 3.2.1).

4. DISCUSSION

4.1 Comparison of Results: Accelerated Corrosion Testing Against Immersion Testing on Bare Tungsten Alloys

Accelerated storage trials are the main source of information on the factors that determine safe service life. However, it is difficult to relate accelerated trials to the real environment as for example the elevated temperature and/or elevated relative humidity may be a severe over-test. The importance of taking these factors into consideration when discussing results from these tests is apparent. The accelerated tests which are referred to in this paper have been selected with these limitations in mind.

Because extreme conditions were not used in the accelerated tests conducted in this study, it would seem reasonable to anticipate that the results of the Cyclic Humidity Test and those for immersion in distilled water [4] would form one consistent family of results, while those for the Salt Mist Test and immersion in sodium chloride solution [4] would form another. In broad terms this is the case (see Table 3). For example, in the "distilled water family" the corrosion products are rich in tungsten (i.e. tungsten grain phase is readily attacked together with the binder phase) while those of the "sodium chloride family" are rich in binder elements (i.e. binder phase is attacked more readily than the tungsten grain phase). Thus the mode of attack on the surface within each family of tests is similar. The above latter mode of attack is the more insidious, for in this case penetration in the grain boundary areas will exceed the calculated penetration rates. This type of attack can result in loss of strength and ductility.

However, inconsistencies arise within each family when the results are compared in fine detail. Consider, for example, corrosion rates (Table 3):

| | | |
|--------------------------|---------|-----------------|
| Distilled water | AUS < W | distilled water |
| Cyclic Humidity Test | AUS > W | family |
| Sodium chloride solution | AUS > W | sodium chloride |
| Salt Mist Test | AUS < W | family |

Similarly, for the two tests within each family, the trend in the corrosion rates does not follow the same sequence. For example, the corrosion rate in the Cyclic Humidity Test is about five times that for immersion in distilled water for all the alloys except UK (Fe) where the two rates are approximately equal. Both sets of tests did show, however, that pure tungsten is moderately corrosion resistant and that those alloys containing copper have the highest corrosion rates.

4.2 Corrosion Mechanism

The corrosion processes are complex and from the present work are not completely understood: however, some comments can be made. (In the following discussion (W-Cu) designates tungsten alloys free of copper while (W + Cu) means alloys containing copper.)

For the distilled water/Cyclic Humidity Tests it appears that the corrosion is essentially a bimetallic or galvanic reaction, with the tungsten grains and the binder phase acting as electrodes. Inspection of the corrosion products indicates that for (W-Cu) alloys the binder phase is anodic with respect to the tungsten grains (i.e. the corrosion products contain a high percentage of elements from the binder phase) whereas for (W + Cu) alloys the polarity is reversed and it is the tungsten grains which are preferentially attacked. Also in these tests the AUS alloy had the lowest corrosion rate, even lower than the copper-free UK alloy, and this may be attributed to reduced galvanic effects associated with less binder phase being present in the AUS alloy.

The effects of chloride ions are not well understood. Using the galvanic model it is apparent that when chloride ions are present the binder is anodic with respect to the tungsten grains for both the (W-Cu) and (W + Cu) alloys, being more anodic for the (W-Cu) alloys. However, for the (W + Cu) alloys the corrosion rate is greater (Table 2) indicating that other corrosion mechanisms are also occurring.

In distilled water tungsten readily corrodes, while in the Cyclic Humidity Test it was immune to corrosion. This is attributed to differences in oxygen availability to the surfaces. In the Cyclic Humidity Test oxygen can readily diffuse to the surface but this diffusion would be hindered in solution. It is suggested that the role of oxygen is to form and maintain a continuous corrosion-resistant oxide layer on the surface of the tungsten.

In the previous report [4] crevice attack was found to occur on (W-Cu) alloys although the mechanism of this attack was not understood. By extending the corrosion-resistant oxide film model to (W-Cu) alloys, a crevice effect could be predicted for these alloys (cf. susceptibility to crevice corrosion attack of stainless steels). With (W + Cu) alloys it is considered that, because of their high corrosion rates, a protective oxide film is not so readily formed and hence they are not susceptible to crevice corrosion.

4.3 Corrosion Testing of Encapsulated Penetrators

Cyclic Humidity Tests conducted on the encapsulated penetrators indicated that the encapsulation by itself was not enough to protect the enclosed tungsten alloy AUS from corrosion in the warm damp environment of the test. The combination of encapsulation and a well-sealed steel ammunition box was, however, adequate under the conditions of this test. On the other hand, if the encapsulated round is exposed to the test environment for a short period and then stored in the above well-sealed container incorporating that environment, corrosion of the underlying tungsten alloy will again occur. Further, the rate under these circumstances is identical with that obtained for encapsulated rounds that are not boxed.

4.4 Significance of the Work to Australian Defence

The selection of the Cyclic Humidity Test as the principal accelerated test was because ammunition can spend the major part of its life confined in a package which may be stored in a range of locations and subjected to temperature fluctuations. Further it is understood from the Naval R and D Requirements Committee that they prefer not to use special packaging procedures for this ammunition.

Cognizance was also taken of the fact that in service conditions the ammunition may be exposed to natural climatic conditions and then stored for an extended period. It is, therefore, not unrealistic to assume (i) that at some stage during its life-span the ammunition will be exposed to air saturated with water vapour and that water will condense on its surfaces or (ii) that it will be subjected to direct rain fall.

Consider, for example, ammunition in the Phalanx gun where Figure 6 shows that this ammunition is exposed to the environment. After training exercises such contaminated ammunition could be returned to its ammunition box and, as a consequence, moisture could be introduced into the sealed box. This ammunition could then be subjected to long-term storage in this environment.

A common requirement for Australian Defence materiel is that it must be able to undergo storage for at least twenty years. However the work above indicates that unless special precautions are taken, such as hermetically sealing the ammunition in a steel container, some corrosion will take place during long-term storage in packages. This is particularly true for ammunition that is used in a trial and then re-packaged. It is yet to be determined whether this corrosion will be unacceptable, for it is difficult to translate the laboratory accelerated corrosion tests into a realistic assessment of the amount of corrosion likely to occur during the long-term storage. The normal procedure is to rely on experience.

A second and no less difficult task is in predicting the effects of realistic corrosion, with associated defects and corrosion products, on ballistic performance. For example, how much corrosion will be enough to (i) interfere with the reliable stripping of the sabot after the round has left the muzzle, (ii) alter the aerodynamic flow over the surface with the possibility of causing the projectile to yaw or tumble, (iii) cause a reduction in ballistic accuracy due to a shift in the centre of gravity of the penetrator, (iv) cause the sabot to swell and cause the round to jam in the gun, (v) embrittle the penetrator so that it would break-up due to stress corrosion cracking either upon firing or on hitting the target?

As the Australian Navy plans to use the tungsten alloy AUS for the Phalanx system well into the future, the outcome of this investigation is of some significance. The extensive tests so far have indicated that compared with the other alloys tested, the Australian alloy has the best resistance to corrosion.

This work emphasizes the need to study the resistance to corrosion of equipment, and it is generally accepted that this resistance must be introduced at the design stage of the equipment. It must not be left as an afterthought to be tackled when the equipment is in service. However, a vital consideration is whether any correlation exists between the results of accelerated corrosion tests and the actual life of equipment in the real operational environment. In practice, such correlation as there might be is largely based on experience and professional judgement.

There is no doubt that properly selected accelerated corrosion testing can provide valuable assurance that the equipment will remain both safe and suitable for service during its defined service life. It is a cost-effective method of ensuring that equipment will be in service for its design life. Its success depends on using the appropriate experimental conditions (temperature, humidity, salt, and so on), the translation of these conditions into an appropriate test programme and finally the analysis of the test results.

5. CONCLUSIONS

From the principal findings of this investigation, these conclusions are derived:

- (a) Some corrosion of tungsten penetrators will occur during long-term storage in an uncontrolled environment.
- (b) When corrosion does occur, attack on the binder phase could result in loss of strength and ductility of the rounds.
- (c) The effect of incorporating copper into the alloy results in a decrease of corrosion resistance in cyclic humidity and in salt-mist environments. A similar trend persists on immersion in distilled water and salt-solution environments.
- (d) From the information developed in this investigation, primarily that derived from cyclic temperature-humidity tests, it is estimated that freedom from damaging corrosion for ammunition penetrators made from the tungsten alloy AUS will be for a period of at least twenty years if they are effectively encased for absolute minimal ingress of moisture. This conclusion is particularly pertinent to the storage of tungsten penetrators where made-up rounds may be stored in well-sealed containers with a strictly limited moisture access.
- (e) As lack of condensation cannot be guaranteed under normal use and storage conditions where special precautions are not taken in the packaging procedures, some form of protection will need to be applied to the rounds if they are to withstand normal long-term storage and still be in pristine condition at the end of the storage period.

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TABLE 1

RESULTS OF THE CYCLIC HUMIDITY TEST

| Sample | Weight Loss of Duplicate Samples (mg) | Corrosion Rate | | Corrosion Products | | Scanning Electron Microscope Examination of the Corroded Surfaces |
|-------------------------------------------------|------------------------------------------------|------------------------------------------|--------|-------------------------------------------|---------------------------|-------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------|
| | | mg cm ⁻² day ⁻¹ | mil/yr | Colour | Composition: | |
| | | | | | metal ions only (wt %) | |
| | | | | | W Ni Fe Cu Co | |
| AUS (3.5 Ni, 1.5 Fe) | 14 | 0.040 | 0.3* | Brown, | 76 17 7 | Some tungsten particles still have polishing marks while the surfaces of others have been attacked leaving the binder phase standing proud (see Fig. 2(a)). Thus main attack is on the tungsten particles. |
| | 56 | 0.161 | 1.2 | adherent | | |
| US (1.6 Ni, 0.7 Fe, 0.5 Cu, 0.1 Co) | 943 | 1.380 | 10.3 | Dark | 91 5 2 1.5 0.5 | Some polishing marks still on a few tungsten particles, but in general both the tungsten surface and the binder phase have been extensively attacked (see Fig. 2(b)). |
| | 976 | 1.434 | 10.7 | crystalline on sample and in beaker | | |
| UK (Fe) (5 Ni, 5 Fe) | 123 | 0.147 | 1.1 | Brown | 77 11 12 | No polishing marks are evident on the tungsten particles (see Fig. 2(c)). Both the surface of the tungsten particles and the binder phase have been attacked. Further, some tungsten particle loss has occurred. Thus both the primary tungsten particles and the binder phase have been attacked. |
| | 133 | 0.161 | 1.2 | speckled, adherent | | |

TABLE 1
(continued)

| Sample | Weight Loss of Duplicate Samples (mg) | Corrosion Rate | | Corrosion Products | | Scanning Electron Microscope Examination of the Corroded Surfaces |
|--------------------------------|------------------------------------------------|------------------------------------------|--------|---------------------------------------------------------|-------------------------------------------|-------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------|
| | | mg cm ⁻² day ⁻¹ | mil/yr | Colour | Composition: metal ions only (wt %) | |
| | | | | | W Ni Fe Cu Co | |
| UK (Cu) (7.5 Ni, 2.5 Cu) | 968 | 1.059 | 7.9 | Grey/green crystalline on sample and in beaker | 90 8 2 | It is evident in Fig. 2(d) that while some tungsten particles are still present, others have disappeared. Tungsten particle loss has occurred, leaving behind a honey-comb structure of the binder phase standing proud of the tungsten particles. Further, there has been grain boundary attack on some of the tungsten particles. |
| | 958 | 1.032 | 7.7 | | | |
| W | 0 | 0 | 0 | Pristine condition | | |
| | 0 | 0 | 0 | | | |

* Because of the discrepancy in these corrosion rates, this test was repeated on several different samples with the following results:

Corrosion rates (mil/yr) : 1.7, 0.9, 1.1, 1.1, 0.8, 0.8, 0.9, 0.9, 0.7, 0.8.
Average corrosion rate : 1.0 mil/yr or 0.134 mg cm⁻² day⁻¹.

TABLE 2

RESULTS OF THE SALT MIST TEST

| Sample | Weight Loss of Duplicate Samples (mg) | Corrosion Rate | | Corrosion Products | | Scanning Electron Microscope Examination of the Corroded Surfaces |
|-------------------------------------------------|------------------------------------------------|------------------------------------------|--------|-------------------------------------------|---------------------------|-----------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------|
| | | mg cm ⁻² day ⁻¹ | mil/yr | Colour | Composition: | |
| | | | | | metal ions only (wt %) | |
| | | | | | W Ni Fe Cu Co | |
| AUS (3.5 Ni, 1.5 Fe) | 3 | 0.013 | 0.1 | Areas of orange- brown deposit | 38 35 27 | <u>For all samples</u> Some polishing marks are still visible on tungsten particles but the tungsten surface has been attacked. The binder phase has been extensively attacked. Tungsten particles are standing proud of the binder phase (see Fig. 4). |
| | 2 | 0.013 | 0.1 | | | |
| JS (1.6 Ni, 0.7 Fe, 0.5 Cu, 0.1 Co) | 12 | 0.040 | 0.3 | Green and brown spotted deposit | 57 23 12 6 1.3 | |
| | 18 | 0.067 | 0.5 | | | |
| UK (Fe) (5 Ni, 5 Fe) | 12 | 0.027 | 0.2 | Extensive areas of brown deposit | 29 29 42 | |
| | 10 | 0.027 | 0.2 | | | |
| UK (Cu) (7.5 Ni, 2.5 Cu) | 7 | 0.013 | 0.1 | Green spotted deposit | 72 21 7 | |
| | 7 | 0.013 | 0.1 | | | |
| W | 6 | 0.027 | 0.2 | Grey stains | | |
| | 7 | 0.040 | 0.3 | | | |

TABLE 3

COMPARISON OF THE CORROSION BEHAVIOUR OF THE TUNGSTEN ALLOYS
IN THE VARIOUS TEST ENVIRONMENTS

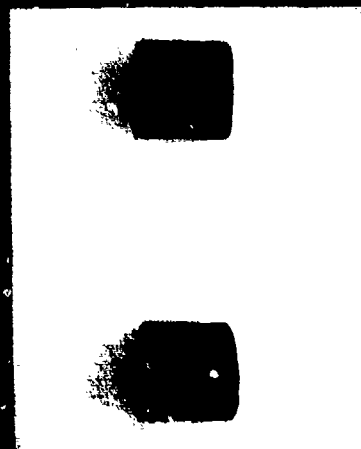
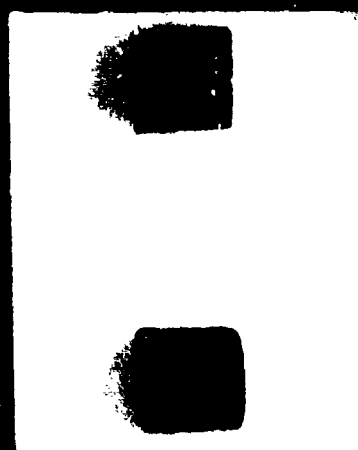
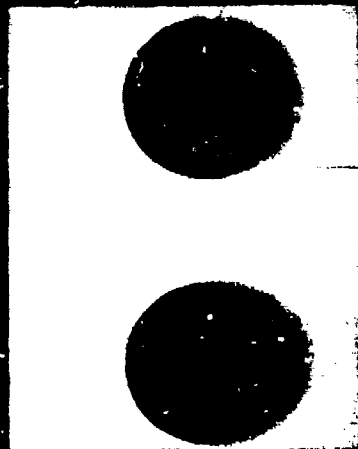
| SAMPLE | DISTILLED WATER FAMILY SET OF TESTS | | | | SODIUM CHLORIDE FAMILY SET OF TESTS | | | |
|---------|-------------------------------------|---------------------------------------|-------------------------|----------------------------------------|-------------------------------------|---------------------------------------|-------------------------|---------------------------------------|
| | Immersion Testing | | Cyclic Humidity Test | | Immersion Testing | | Salt Mist Test | |
| | Corrosion rate (mil/yr) | Tungsten in corrosion products (wt %) | Corrosion rate (mil/yr) | Tungsten in corrosion products (wt %) | Corrosion rate (mil/yr) | Tungsten in corrosion products (wt %) | Corrosion rate (mil/yr) | Tungsten in corrosion products (wt %) |
| A15 | 0.2 | 66 | 1.0 | 76 | 0.2 | <50 | 0.1 | 38 |
| | | Red/brown adherent film | | Light brown | | Fluffy, light brown | | Orange/brown |
| US | 1.9 | >90 | 10.5 | 91 | 0.5 | <60 | 0.4 | 57 |
| | | Black film | | Dark crystalline deposit and droppings | | Fluffy, light brown | | Green and brown |
| UK (Fe) | 1.1 | >80 | 1.15 | 77 | 0.2 | <50 | 0.2 | 29 |
| | | Black film | | Brown | | Fluffy, light brown | | Orange/brown |
| UK (Cu) | 2.5 | >90 | 7.8 | 90 | 0.3 | <60 | 0.1 | 72 |
| | | Brown film | | Grey/green deposit and droppings | | Full grey film | | Light green |
| V | 0.65 | - | 0 | - | 0.02 | - | 0.25 | - |
| | | Speckled dark grey film | | Pristine condition | | Pristine condition | | Dark grey stains |

FIGURE 1 (next page)

State of tungsten alloys and tungsten itself after exposure to the warm, damp conditions created by the Cyclic Humidity Test (56 cycles).

TUNGSTEN ALLOY CORROSION TRIAL

Humidity Test BS 2911, Test 95, Temperature 25°C





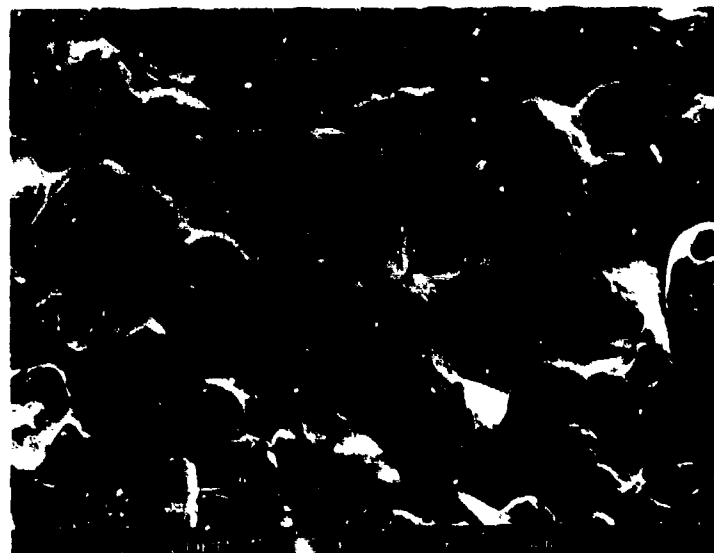
(a)



(b)

FIGURE 2 SEM micrographs of the surfaces of tungsten alloys after exposure to the warm, damp conditions created by the Cyclic Humidity Test (56 cycles) and after removal of the corrosion products.

| | | |
|--------|-------------|-------------|
| Alloys | (a) AUS | (b) US |
| | (c) UK (Fe) | (d) UK (Cu) |



(c)



(d)

FIGURE 2 SEM micrographs of the surfaces of tungsten alloys after exposure to the warm, damp conditions created by the Cyclic Humidity Test (56 cycles) and after removal of the corrosion products.

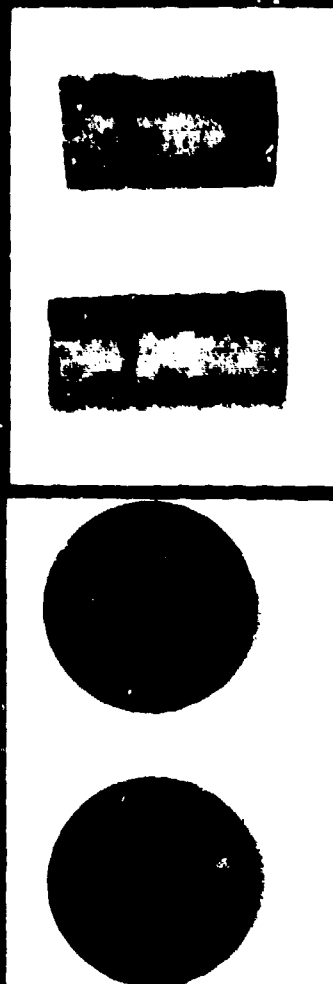
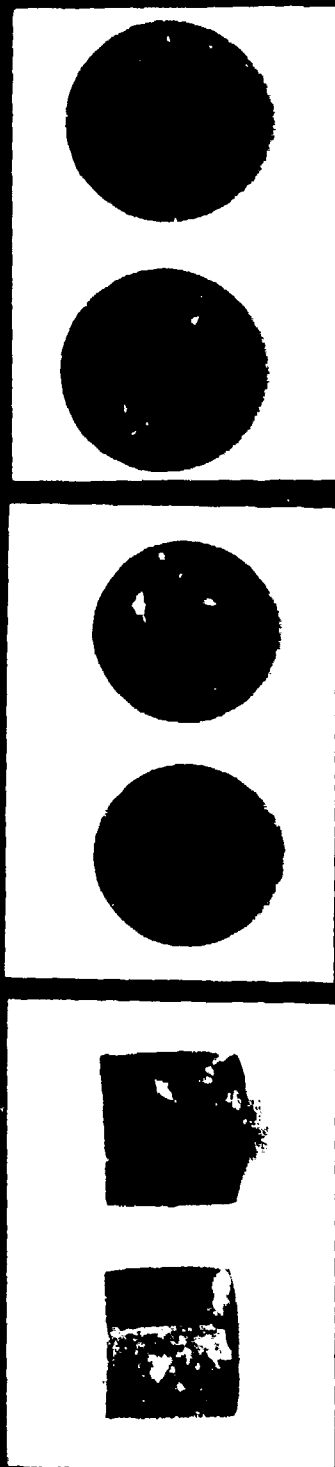
| | | |
|--------|-------------|-------------|
| Alloys | (a) AUS | (b) US |
| | (c) UK (Fe) | (d) UK (Cu) |

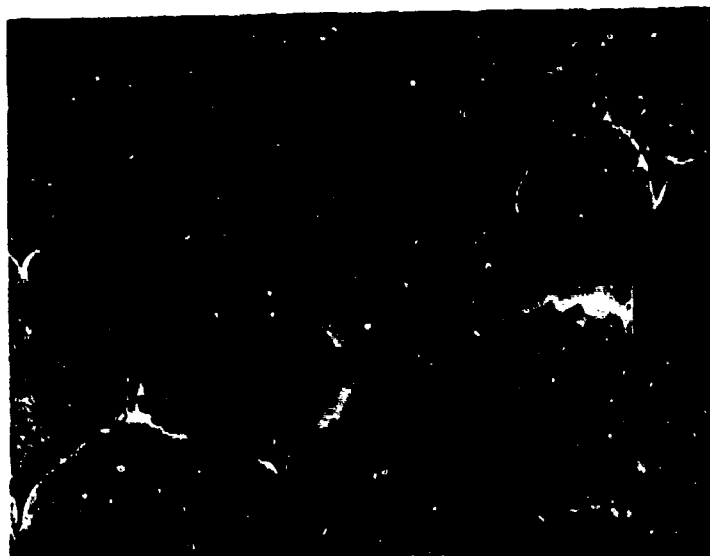
FIGURE 3 (next page)

**State of tungsten alloys and tungsten itself after exposure to the
Salt Mist Test for 28 days.**

7
TUNGSTEN ALLOY CORROSION TRIAL

500 M 3000 8 25 2010 1000





(a)



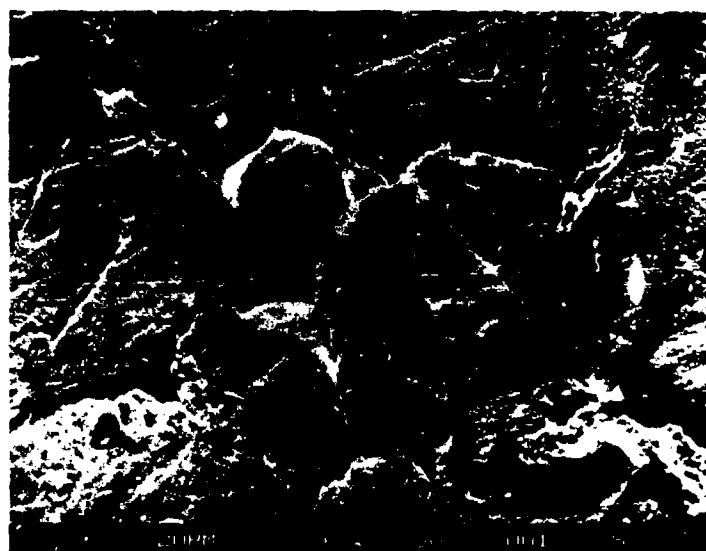
(b)

FIGURE 4 SEM micrographs of the surfaces of tungsten alloys after exposure to the Salt Mist Test for 28 days and after removal of corrosion products.

| | | |
|--------|-------------|-------------|
| Alloys | (a) AUS | (b) US |
| | (c) UK (Fe) | (d) UK (Cu) |



(c)

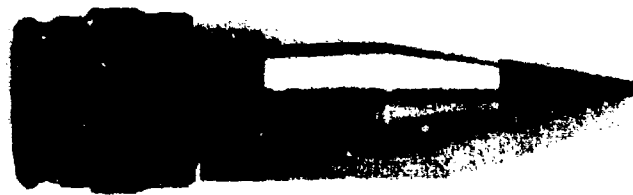


(d)

FIGURE 4 SEM micrographs of the surfaces of tungsten alloys after exposure to the Salt Mist Test for 28 days and after removal of corrosion products.

| | | |
|--------|-------------|-------------|
| Alloys | (a) AUS | (b) US |
| | (c) UK (Fe) | (d) UK (Cu) |

TUNGSTEN ALLOY CORROSIVITY TRIAL
HUMIDITY TRIAL ON ENCAPSULATED PENETRATORS:
BS 2011 TEST D6 (DAMP HEAT CYCLIC) FOR 56 DAYS



(a)

Rounds in ammunition box



(b)

In sealed
box for
all cycles



(b)

Lid off
box for
cycles 3-6



(c)

Rounds not in ammunition box

KEY

- (a) ENCAPSULATED REFERENCE
ROUND (NOT EXPOSED)
- (b) PENETRATOR AFTER TEST
(ENCAPSULATION REMOVED)
- (c) PENETRATOR AFTER CORROSION
PRODUCTS REMOVED



(b)



(c)

FIGURE 5 Cyclic humidity testing of
encapsulated penetrators.

10
mm

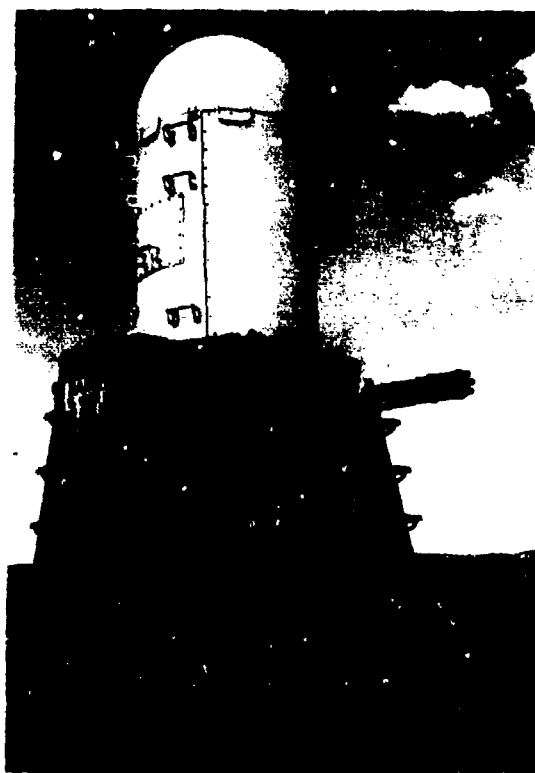


FIGURE 6 The Phalanx Close-in Weapon System. Note the ammunition is exposed to the external environment.

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Part 2: Accelerated corrosion testing

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ABSTRACT

As a consequence of corrosion during long-term storage in uncontrolled environments, where high humidity may be combined with cyclic temperature changes, some high-density sintered tungsten penetrators have been found to be unreliable. A storage life of twenty years without special storage conditions is a requirement for this ammunition, and therefore there is a need to determine the long-term storage capability of selected alloys.

The corrosion behaviour of four candidate alloys has been evaluated and compared with that of pure tungsten. Rates of corrosion during the Cyclic Humidity Test and the Salt Mist Test were ascertained from weight loss measurements. Insight into the corrosion mechanism was gained from the nature of the corrosion products and an examination of the corroded surfaces. In the tests, the alloy 95% W, 2.5% Ni, 1.5% Fe was the most corrosion resistant. The data showed that copper as an alloying element accelerates corrosion of tungsten alloys. Both attack on the tungsten particles and the binder phase were observed together with tungsten grain loss.

The propensity of the above alloy to corrode when encapsulated and also when enclosed by its ammunition box was also evaluated. Conclusions and recommendations regarding the corrosion of tungsten alloy penetrators for use in ammunition are offered.

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